307. *Derivatives of Naphthalene-2 : 3-dicarboxylic Acid.*

By Wilson Baker.

Nitration of naphthalene-2 : 3-dicarboxylic acid with concentrated nitric acid at 100° gives 5-nitronaphthalene-2 : 3-dicarboxylic acid, from which 5-*aminonaphthalene*-2 : 3-*dicarboxylic acid* is obtained by reduction with ferrous sulphate and ammonia. This base reacts in position 8 with diazonium salts in acid solution to yield aminoazo-compounds, reduction of which with stannous chloride and hydrochloric acid yields 5 : 8-*diaminonaphthalene*-2 : 3-*dicarboxylic acid.* The orientation of these substances follows from the fact that the aminoazo-compounds, if sufficiently soluble in water, may be diazotised and coupled with phenolic compounds to give bisazo-dyes. The aminoazo-compounds from 5-aminonaphthalene-2 : 3-dicarboxylic acid and diazotised aniline or sulphanilic acid were insufficiently soluble for this purpose, but diazotised β-naphthylamine-6 : 8-disulphonic acid yielded an aminoazo-compound which was further diazotised and coupled with both β-naphthol-3 : 6-disulphonic acid and 1-amino-8-naphthol-3 : 6-disulphonic acid. The formation of these bisazo-dyes precludes the possibility of the amino-group being in position 6, since this would give an *o*-aminoazo-compound incapable of diazotisation. The only other possibility is position 1, but nitration of naphthalene-2 : 3-dicarboxylic acid in this position is very unlikely, and the corresponding 1-aminonaphthalene-2 : 3-dicarboxylic acid would not be expected to couple readily with diazonium salts, nor would the aminoazo-compound be likely to be capable of ready diazotisation.

Nitration of napththalene-2 : 3-dicarboxylic acid in sulphuric acid gives a dinitro-derivative, probably either 5 : 6- or 1 : 5-*dinitronaphthalene*-2 : 3-*dicarboxylic acid.*

A number of *N*-substituted imides of 5-nitronaphthalene-2 : 3-dicarboxylic acid and of 4-nitrophthalic acid are described.

Experimental.

5-*Nitronaphthalene*-2 : 3-*dicarboxylic Acid.*—Finely powdered naphthalene-2 : 3-dicarboxylic acid (10 g.) and nitric acid (30 c.c.; *d* 1·42) were heated at 100° for 1 hour with occasional shaking. The sandy product (11·5 g.) was collected after the addition of water, washed, and crystallised from 50% acetic acid (350 c.c.). It formed pale yellow, prismatic needles, m. p. about 238° with slight previous softening and formation of the anhydride (Found : C, 54·8; H, 2·5; N, 5·4; equiv., 130·0. $C_{12}H_7O_6N$ requires C, 55·2; H, 2·7; N, 5·3%; equiv., 130·5). The *anhydride,* best prepared by boiling the acid with acetic anhydride for 1 hour, separated from acetic anhydride in pale yellow, irregular prisms, m. p. 208° (Found : N, 5·8. $C_{12}H_5O_5N$ requires N, 5·8%). The *imide,* from the anhydride (8·1 g.) and urea (2 g.) at about 200°, separated from pyridine in pale yellow, flat prisms containing solvent of crystallisation which was lost on digestion with warm benzene; m. p. 300° (Found in material dried at 100° in a vacuum : N, 11·2. $C_{12}H_6O_4N_2$ requires N, 11·6%). The *phenylimide,* from the acid (1 g.) and aniline (2 c.c.) for 5 minutes at the b. p., followed by addition of benzene, separated from benzene, in which it was very sparingly soluble, in pale yellow, feathery crystals, m. p. 232° (Found : N, 8·6. $C_{18}H_{10}O_4N_2$ requires N, 8·8%). The p-*nitrophenylimide,* prepared by slowly heating an intimately powdered mixture of the acid (5·2 g.) and *p*-nitroaniline (10·4 g.) to 250°, and subsequently digesting the crushed mass with warm dilute hydrochloric acid to remove the excess of *p*-nitroaniline, separated from boiling glacial acetic acid, in which it was exceedingly sparingly soluble, in fine needles, m. p. 254° (Found : N, 11·5. $C_{18}H_9O_6N_3$ requires N, 11·6%).

Dinitronaphthalene-2 : 3-*dicarboxylic Acid.*—Naphthalene-2 : 3-dicarboxylic acid (2 g.) in concentrated sulphuric acid (5 c.c.) was treated with nitric acid (2 c.c.; *d* 1·42) in concentrated sulphuric acid (5 c.c.), and after several hours the solution was diluted and the product collected. It separated from hot water in thin needles, m. p. 254° (Found : N, 9·3; equiv., 156. $C_{12}H_6O_8N_2$ requires N, 9·3%; equiv., 153). When boiled with a 3% alcoholic solution of hydrogen chloride for 6 hours, it gave the *monoethyl* ester as prisms, containing alcohol of crystallisation which was lost at 100°, m. p. 229° (Found : N, 8·7. $C_{14}H_{10}O_8N_2$ requires N, 8·4%).

5-*Aminonaphthalene*-2 : 3-*dicarboxylic Acid.*—To a solution of 5-nitronaphthalene-2 : 3-dicarboxylic acid (14 g.) in aqueous ammonia (100 c.c. of aqueous ammonia, *d* 0·88; 300 c.c. of water) was added a hot solution of crystallised ferrous sulphate (122 g.) in water (200 c.c.), and the mixture heated on the steam-bath for ½ hour. The product was filtered whilst hot, and addition of acetic acid (50 c.c.) to the filtrate precipitated a flocculent mass which subsequently became crystalline and was collected after 12 hours (8·5 g.). It crystallised from 75% acetic acid, in which it was very sparingly soluble, in fine needles, m. p. above 360° (Found : N, 4·9. $C_{12}H_9O_4N,C_2H_4O_2$ requires N, 4·8%). Its solution in acetic acid shows a weak green fluorescence in ultra-violet light. 5-*Acetamidonaphthalene*-2 : 3-*dicarboxylic anhydride* (acetic anhydride for ¼ hour at the b. p.) formed small needles, m. p. 290° (darkening; rapid heating) (Found : C, 65·9; H, 3·6. $C_{14}H_9O_4N$ requires C, 65·9; H, 3·5).

5 : 8-*Diaminonaphthalene*-2 : 3-*dicarboxylic Acid.*—5-Aminonaphthalene-2 : 3-dicarboxylic acid (6·93 g.; 1 mol.) was dissolved in a hot mixture of concentrated hydrochloric acid (18 c.c.) and water (100 c.c.), and the rapidly cooled solution added to a solution of benzenediazonium chloride (aniline, 2·79 g.; *N*-hydrochloric acid, 90 c.c.; 2% sodium nitrite solution, 103·5 c.c.) at 0°. Coupling occurred on the addition of crystallised sodium acetate (90 g.), and the deep-violet, flocculent product was collected after a few hours. This aminoazo-compound was now warmed with alcohol and excess of stannous chloride in concentrated hydrochloric acid until the deep colour faded. The diluted solution was treated with excess of hydrogen sulphide, the filtrate evaporated to dryness in a vacuum, and the crystalline residue washed with boiling water to remove aniline hydrochloride. 5 : 8-*Diaminonaphthalene*-2 : 3-*dicarboxylic acid* formed minute yellow prisms, which did not melt but decomposed at high temperatures (Found in material dried at 100° in a vacuum : N, 9·8. $C_{12}H_{10}O_4N_2,2H_2O$ requires N, 9·9%). The hydrochloride separated from somewhat dilute hydrochloric acid in small crystals, which yielded the free base on treatment with water.

5-*Amino*-8-p-*sulphobenzeneazonaphthalene*-2 : 3-*dicarboxylic Acid.*—This was prepared by coupling diazotised sulphanilic acid with 5-aminonaphthalene-2 : 3-dicarboxylic acid, as described above. The deep-red pasty mass was diluted after several hours, excess of hydrochloric acid added, and the whole heated to 80°, the flocculent violet product being converted into an almost black, microcrystalline powder with a green reflex. This was washed with hot water and dried in a vacuum at 100° (Found : N, 9·7. $C_{18}H_{11}O_7N_3S,H_2O$ requires N, 9·7%); its alkaline solutions were intensely orange.

Bisazo-dyes derived from 5-Aminonaphthalene-2 : 3-dicarboxylic Acid.—Sodium β-naphthylamine-6 : 8-disulphonate (8·6 g.) was diazotised and treated with 5-aminonaphthalene-2 : 3-dicarboxylic acid (6·2 g.) as above. The mixture was stirred for 2 hours in the cold, and after addition of sodium acetate (50 g.), warmed to 50° and treated with excess of acetic acid. The deep-violet product was collected, washed, dissolved in water (200 c.c.) and concentrated hydrochloric acid (12·5 c.c.), and treated with sodium nitrite (1 g.) in water at 10°, the resulting brown solution being kept for 12 hours at 0° and divided into two portions. These were treated with 4·3 g. of the sodium salts of (i) β-naphthol- and (ii) 1-amino-8-naphthol-3 : 6-disulphonic acids dissolved in water (100 c.c.) containing sodium carbonate (30 g.), and then stirred for 2 hours, heated to 80°, cooled, saturated with sodium chloride, and the almost black, crystalline products collected. The bisazo-dye from (i) gave an intensely violet solution in water, which became indigo-blue on the addition of sodium hydroxide, whilst that from (ii) gave an exceedingly intense Prussian-blue solution; they could not be obtained in an analytically pure condition.

4-*Nitrophthalo*-p-*nitrophenylimide.*—4-Nitrophthalic acid (6·3 g.) and *p*-nitroaniline (4·1 g.) were powdered, and heated (oil-bath at 200°) for 10 minutes. The product separated from acetic acid (500 c.c.) in colourless prisms (6·1 g.), m. p. 253° (Found : C, 54·0; H, 2·5; N, 13·5. $C_{14}H_7O_6N_3$ requires C, 53·7; H, 2·2; N, 13·4%).

4-*Nitrophthalo*-p-*acetamidophenylimide.*—Powdered 4-nitrophthalic acid (6·3 g.) and *p*-aminoacetanilide (4·5 g.) were heated to 250° during 20 minutes. The product was crystallised twice from glacial acetic acid (600 c.c.) and formed thin, yellow, prismatic needles (5·7 g.), m. p. 295° (partial decomp.) (Found : C, 59·3; H, 3·5; N, 12·7. $C_{16}H_{11}O_5N_3$ requires C, 59·1; H, 3·4; N, 12·9%).

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